

BRL R 1429

# BRL

AD687269

REPORT NO. 1429

## A CLASS OF TWO-PHASE STATE EQUATIONS

by

G. D. Kahl

March 1969

This document has been approved for public release and sale;  
its distribution is unlimited.

U.S. ARMY ABERDEEN RESEARCH AND DEVELOPMENT CENTER  
BALLISTIC RESEARCH LABORATORIES  
ABERDEEN PROVING GROUND, MARYLAND

Destroy this report when it is no longer needed.  
Do not return it to the originator.

The findings in this report are not to be construed as  
an official Department of the Army position, unless  
so designated by other authorized documents.

BALLISTIC RESEARCH LABORATORIES

REPORT NO. 1429

MARCH 1969

A CLASS OF TWO-PHASE STATE EQUATIONS

G. D. Kahl

Exterior Ballistics Laboratory

This document has been approved for public release and sale;  
its distribution is unlimited.

RDTE Project No. 1T061102A33D

ABERDEEN PROVING GROUND, MARYLAND

# BALLISTIC RESEARCH LABORATORIES

REPORT NO. 1429

GDKahl/so  
Aberdeen Proving Ground, Md.  
March 1969

## A CLASS OF TWO-PHASE STATE EQUATIONS

### ABSTRACT

The properties of a particular class of elementary, two-phase state equations are found to be simply related. The class includes some familiar equations, such as the Van der Waals, Berthelot, and Clausius types, as well as a form recently suggested by J. J. Martin. Conditions for stable equilibrium are given, and some examples are compared. A table of values is included which can be used with elementary transformations to find the equilibrium coexistence properties of any member of the set. A drawback for this type equation along the critical isotherm is noted.

# TABLE OF CONTENTS

	Page
ABSTRACT . . . . .	3
LIST OF ILLUSTRATIONS . . . . .	7
I. INTRODUCTION . . . . .	9
II. TRANSFORMATION . . . . .	11
III. EXAMPLES . . . . .	15
A. Coexistence Boundary . . . . .	15
B. Vapor Pressure ( $\gamma \leq 1$ ) . . . . .	18
C. Heat of Vaporization . . . . .	18
D. Specific Heat at Constant Volume . . . . .	21
E. Vaporizing Signal Speed . . . . .	23
IV. DISCUSSION . . . . .	24
FOOTNOTES AND REFERENCES . . . . .	27
APPENDIX. . . . .	29
DISTRIBUTION LIST. . . . .	33

# LIST OF ILLUSTRATIONS

	Page
Figure	
1. Reduced temperature vs. saturation densities . . . . .	17
2. Vapor pressure vs. temperature . . . . .	19
3. Latent heat of vaporization vs. reduced temperature . .	20
4. Vaporizing signal speed of the saturated liquid . . . .	26
Table	
I. Functions for typical state equations of the class . . .	16
II. Critical point values . . . . .	25
III. Reduced values of coexistence temperature, saturation densities, and vapor pressure for the Van der Waals-Maxwell state equation . . . . .	30

## I. INTRODUCTION

There exists a substantial number of elementary pressure state equations which predict a liquid-vapor phase transition and a critical point. It is the purpose of this paper to show that many of these, though not all, belong to a single class, and that the various thermodynamic predictions between class members are simply related. Some familiar equations belong to this group, including the Van der Waals-Maxwell, [V-M], equation, which will serve as the basis for comparison. A direct method can be demonstrated relating the limiting values of thermodynamic quantities in the critical region.

The form of equation treated here is

$$P(V,T) = (RT/[V-b(T)]) - a(T)/[V+c(T)]^2 \quad (1)$$

where  $V \geq b(T) > -c(T)$ , and  $T > 0$ ;  $P$ ,  $V$ , and  $T$  are pressure, specific volume and temperature, respectively.  $R$  is the gas constant, and  $a(T)$ ,  $b(T)$  and  $c(T)$  are analytic functions of positive  $T$ . Some restrictions are needed on the latter functions. For instance,  $b(T)$  is assumed to be positive and larger than  $-c(T)$ ; and  $a(T)$  must be positive for all  $T$  less than some value exceeding the critical temperature,  $T_c$ , in order to produce a critical point. It is shown in the Appendix that  $b(T)$  must be a constant, which is henceforth assumed.

Eq. (1) is expressed in reduced form by use of the scaled variables  $\beta \equiv P/P_c$ ,  $\gamma \equiv T/T_c$ ,  $\eta \equiv 1/\alpha \equiv V/V_c$  (this notation corresponds to that of Reference [1], with subscript  $c$  denoting critical value) as

$$\beta(\eta,\gamma) = (1/Z_c) \{ (\gamma/[\eta-B]) - (9/8)A(\gamma)/[\eta+C(\gamma)]^2 \} \quad (2)$$

where  $\eta \geq B > -C(\gamma)$  and  $\gamma > 0$ , and  $Z_c \equiv P_c V_c / (RT_c)$  is the critical compressibility. The transformations from  $a$ ,  $b$ , and  $c$  to  $A$ ,  $B$ , and  $C$  are  $(9/8) A(\gamma) = a(T)/[RT_c V_c]$ ,  $B = b/V_c$  and  $C(\gamma) = c(T)/V_c$ . It follows that  $A(\gamma)$  is positive for a range of  $\gamma$  larger than unity. The variables

$\beta$ ,  $\gamma$ ,  $\eta$  and  $\alpha$  all are unity at the critical point. It is seen that Eq. (1) approximates the ideal gas equation when  $V$  becomes very large.

In order that the state of the system be stable, certain relations must hold for the thermodynamic functions<sup>2†</sup>. These are:  $C_v > 0$ , where  $C_v$  is the specific heat at constant volume; and  $\left(\frac{\partial \beta}{\partial \eta}\right)_\gamma < 0$ , except at the critical point. At the critical point, the conditions become  $\left(\frac{\partial \beta}{\partial \eta}\right)_\gamma = 0 = \left(\frac{\partial^2 \beta}{\partial \eta^2}\right)_\gamma$ .

Imposing these latter conditions at the critical point, one obtains the relations:

$$A_1 = 1+C_1; B_1 = (1/3)(1-2C_1); \text{ and } Z_c = (3/8)/(1+C_1) \quad (3)$$

where a subscript 1 on A, B, or C denotes the value at the critical temperature,  $\gamma = 1$ . Thus, the function  $C(\gamma)$  fixes the critical compressibility,  $Z_c$ .

One observes that for  $\gamma < 1$ , there is a domain of  $(\eta, \gamma)$  where  $\frac{\partial \beta}{\partial \eta}$  from Eq. (2) is positive, contrary to the stability requirement. Thus, Eq. (2) cannot represent a stable thermodynamic pressure function in this domain; instead, the vapor pressure function,  $\beta_A(\gamma)$ , independent of  $\eta$ , replaces Eq. (2) as the pressure function here. The usual method of defining  $\beta_A(\gamma)$  so it is continuous with the  $\beta(\eta, \gamma)$  of Eq. (2) is by means of the Maxwell rule: for any fixed  $\gamma \leq 1$ ,

$$\int_{\eta_3(\gamma)}^{\eta_1(\gamma)} \beta(\eta, \gamma) d\eta = \beta_A(\gamma) \{ \eta_1(\gamma) - \eta_3(\gamma) \}, \quad (4)$$

with

$$\beta(\eta_1, \gamma) = \beta(\eta_3, \gamma) = \beta_A(\gamma) .$$

---

†References are listed on page 27.



The quantities  $\eta_3(\gamma)$  and  $\eta_1(\gamma)$  are points on the saturated liquid and vapor loci, respectively. For any fixed  $\gamma \leq 1$ , the domain  $\eta_3 \leq \eta \leq \eta_1$  is the region where liquid and vapor coexist at the same pressure, temperature, and chemical potential. The boundaries of the coexistence region are also defined by Eq. (4). The use of the Maxwell rule implies that the Helmholtz free energy is a unique analytic function of  $V$  and  $T$  where Eq. (1) is the proper pressure function<sup>3</sup>. With this analyticity, Eq. (4) insures that the pressure and chemical potential are continuous functions of  $V$  and  $T$  across the coexistence boundaries. To avoid confusion, a subscript a will hereafter be used on a thermodynamic variable within the coexistence region, while a subscript s will refer to the value outside coexistence.

## II. TRANSFORMATIONS

For compactness, let

$$f(\gamma) = 3[B+C(\gamma)]/A(\gamma) . \quad (5)$$

For  $\gamma > 1$ ,  $\frac{\partial \beta_a}{\partial \eta}$  must never be positive, or the stability requirement is violated. From Eq. (2),

$$Z_c \frac{\partial \beta_a}{\partial \eta} = - (\gamma/[\eta-B]^2) \{1-G(\eta, \gamma)\}, \quad (6)$$

where

$$G(\eta, \gamma) = (9/4) A(\gamma) [\eta-B]^2 / (\gamma[\eta+C]^3) . \quad (7)$$

Since both  $Z_c$  and  $\gamma$  are positive, Eq. (6) shows  $\frac{\partial \beta_a}{\partial \eta}$  is negative, providing  $G(\eta, \gamma)$  is less than 1 for any  $\eta \geq B$ . This latter condition is easily satisfied when  $A(\gamma)$  is negative; but  $A(\gamma)$  was previously required to be positive for all  $\gamma$  less than some value  $\gamma_0$  exceeding one. In this range of  $\gamma$ , i.e.,  $(0 < \gamma < \gamma_0)$ ,  $G(\eta, \gamma)$  is positive and has a maximum value with respect to  $\eta$ ,  $G_m(\gamma)$ , at  $\eta = 3B+2C(\gamma)$ , where

$$G_M(\gamma) = A(\gamma)/[3\gamma(B+C)] = 1/[\gamma f(\gamma)]. \quad (8)$$

Forcing  $\gamma f(\gamma) > 1$  for  $\gamma_0 > \gamma > 1$  will insure that  $\frac{\partial \beta_B}{\partial \eta}$  is non-positive.

For  $\gamma < 1$ , one wishes to satisfy Eq. (4) in the  $(\eta, \gamma)$  domain of coexistence. The mathematical function  $\frac{\partial \beta(\eta, \gamma)}{\partial \eta}$  of Eq. (2) must therefore have zeros in this domain, so  $\gamma f(\gamma) < 1$  for  $\gamma < 1$ . At  $\gamma = 1$ ,  $\gamma f(\gamma)$  is unity, as may be seen from the relations already given for  $\gamma = 1$ .

Defining

$$X(\gamma) \equiv (3/8)/[Z_c f^2(\gamma)A(\gamma)], \quad (9)$$

and the transformations

$$u(\gamma) \equiv \gamma f(\gamma), \quad (10)$$

$$v(\eta, \gamma) \equiv [\eta + C(\gamma)]/[f(\gamma)A(\gamma)], \quad (11)$$

$$w(\eta, \gamma) \equiv \beta(\eta, \gamma)/X(\gamma), \quad (12)$$

$$w_A(\gamma) \equiv \beta_A(\gamma)/X(\gamma), \quad (13)$$

with the convention that  $w(\eta, \gamma)$  has a subscript a when  $\beta(\eta, \gamma)$  does, one finds that Eq. (2) transforms into

$$w(v, u) = \{8u/(3v-1)\} - 3/v^2. \quad (14)$$

Moreover, for any fixed  $u \leq 1$ , Eq. (4) transforms into

$$\int_{v_3(u)}^{v_1(u)} w(v, u) dv = w_A(u) \{v_1(u) - v_3(u)\} \quad (15)$$

with  $w(v_1, u) = w_B(v_1, u) = w(v_3, u) = w_B(v_3, u) = w_A(u)$ .

Eq. (14) has exactly the form of the reduced Van der Waals pressure function, providing one interprets  $w$ ,  $v$ , and  $u$  as reduced pressure, volume, and temperature respectively. All the functions  $w_B$ ,  $w_A$ ,  $u$ , and  $v$ , are unity at the critical point where  $\eta = 1$  and  $\gamma = 1$ .

The Jacobian,  $J = \frac{\partial(u,v)}{\partial(\gamma,\eta)}$  of the transformations of the independent variables  $\gamma$  and  $\eta$  to the new independent variables  $u$  and  $v$  reduces to  $\frac{\partial v}{\partial \eta} \frac{\partial u}{\partial \gamma}$  because  $u$  is independent of  $\eta$ . Using Eqs. (10) and (11) this Jacobian is

$$J = \{1 + \gamma \frac{df}{d\gamma} / f(\gamma)\} / A(\gamma), \quad (16)$$

and where  $J$  or  $J^{-1}$  is neither zero nor infinite, the mapping is single valued. It will be assumed in the further development that for  $\gamma \leq 1$  this mapping is single valued, so the necessary conditions on  $A(\gamma)$ ,  $B$  and  $C(\gamma)$  to accomplish this purpose will be assumed henceforth. The thermodynamic properties of any state equation of this class for  $\gamma \leq 1$  can now be expressed in terms of those corresponding properties known for the [V-M] system, and the given transformation Eqs. (10-13).

The method for finding the properties in the coexistence region, including their limits at the critical point, is that demonstrated by Barieau<sup>1</sup>. For fixed  $u \leq 1$ , Eq. (14) becomes a cubic polynomial in  $v$ ; one finds from it the largest and smallest values of  $v$  ( $v_1(u)$  and  $v_3(u)$ , respectively) which simultaneously satisfy Eq. (15). Letting  $\xi \equiv 1/v$ , one then obtains, for  $u \leq 1$ ,

$$w_A(\xi_1, \xi_3) = \xi_1 \xi_3 (3 - \xi_3 - \xi_1), \quad (17)$$

$$8u(\xi_1, \xi_3) = (\xi_1 + \xi_3)(3 - \xi_1)(3 - \xi_3). \quad (18)$$

Differentiating both sides of Eq. (15) by  $u$  results in the differential equation:

$$u \frac{dw_A}{du} = w_A + 3\xi_1 \xi_3 = \xi_1 \xi_3 (6 - \xi_3 - \xi_1); \quad (19)$$

similarly differentiating Eqs. (17) and (18), and using Eq. (17) gives one

$$u \frac{d\xi_1}{du} = \xi_1(3-\xi_1)/(3-2\xi_1-\xi_3), \quad (20)$$

$$u \frac{d\xi_3}{du} = \xi_3(3-\xi_3)/(3-2\xi_3-\xi_1). \quad (21)$$

The relation

$$u \frac{d^2 w_A}{du^2} = 3 \frac{d(\xi_1 \xi_3)}{du}, \quad (22)$$

follows directly from Eq. (19). Eqs. (17-22) have the same form as the corresponding ones of Reference [1] used to display properties of the [V-M] fluid, providing  $w_A$ ,  $u$ , and  $\xi$  here are replaced by  $\beta$ ,  $\gamma$ , and  $\alpha$  to conform with the notation there.

Proceeding analogously, and defining  $y \equiv \xi_3 - 1$  and  $x \equiv 1 - \xi_1$ , one can use Eqs. (14), (15), (17) and (18) to obtain  $y$  as a function of  $x$ ; this function can be expanded in the power series

$$y = \sum_{i=1}^{\infty} a_i x^i, \quad (23)$$

where Barieau<sup>1</sup> finds  $a_1=1$ ,  $a_2=1/5$ , and  $a_3=1/25$ . The value of  $a_4$  was subsequently evaluated by the present author to be 19/350.

All quantities  $\xi_1$ ,  $\xi_3$ ,  $w_A$ , etc., (as functions of  $u$ ) have been tabulated previously for the [V-M] system. They may be used to find limiting thermodynamic values in the critical region for any equation of the class considered here; a brief table is in the Appendix.

Some inverse transformations are

$$\eta_j = 1/\alpha_j = v_j f(\gamma) A(\gamma) - C(\gamma), \quad (j=1,3) \quad (24)$$

$$\beta_B(\eta, \gamma) = w_B(v, u)X(\gamma) \quad (25)$$

$$\beta_A(\gamma) = w_A(u)X(\gamma) \quad (26)$$

$$\left\{ \frac{\partial \beta_B(\eta, \gamma)}{\partial \gamma} \right\}_{\eta} = X(\gamma) \left\{ \left( \frac{\partial w_B}{\partial v} \right)_u \left( \frac{\partial v}{\partial \gamma} \right)_{\eta} + \left( \frac{\partial w_B}{\partial u} \right)_v \left( \frac{\partial u}{\partial \gamma} \right)_{\eta} \right\} + w_B(v, u) \frac{dX}{d\gamma} \quad (27)$$

$$\frac{d\beta_A(\gamma)}{d\gamma} = X(\gamma) \left\{ \frac{dw_A}{du} \left( \frac{\partial u}{\partial \gamma} \right)_{\eta} \right\} + w_A(u) \frac{dX}{d\gamma} \quad (28)$$

From Eqs. (27) and (28), it can be seen that  $\left\{ \frac{\partial \beta_B(1,1)}{\partial \gamma} \right\}_{\eta}$  is equal to  $\frac{d\beta_A(1)}{d\gamma}$ , because it is known from the Van der Waals function that at the point  $(v, u) = (1, 1)$ : (a),  $w_B$  and  $w_A$  are each equal to one; (b),  $\left( \frac{\partial w_B(1,1)}{\partial u} \right)_v$  and  $\frac{dw_A(1)}{du}$  are each equal to four; and (c),  $\left( \frac{\partial w_B}{\partial v} \right)_u$  is zero.

Therefore, for any equation of this class, the temperature derivative of the vapor pressure function is continuous at the critical point with that of the critical isometric, in reduced variables. This continuity does not necessarily hold for higher order derivatives.

### III EXAMPLES AND COMPARISONS

When  $A(\gamma)$ ,  $B$  and  $C(\gamma)$  are specified, one can recognize some well-known state equations. Some examples are shown in Table I. Example 6, with  $A(\gamma)$  a linear function of  $\gamma$ , comes from an equation recently suggested by Martin<sup>4\*</sup>. When  $C(\gamma)$  is a constant, as is true for all equations in Table I, one can use the definitions to show that the product  $f(\gamma)X(\gamma)$  is unity. In the following, certain thermodynamic predictions for some of these examples will be compared.

#### A. Coexistence Boundary.

A comparison is made in Figure 1 of the reduced density on the coexistence boundary for the state equations numbered 2, 4, and 6 in

Table I. Example state equations and transformations

a. Shown in the form  $P(V,T) = [RT/(V-b)] - a(T)/(V+c)^2$ , with constants  $a_j$ ,  $b_j$  and  $c_j$  for the number (j) equation. For all shown {except No. (1), where both  $b$  and  $a(T)$  are zero},  $b_j = V_c [1 - 1/(4Z_c)]$  and  $c_j = V_c [-1 + 3/(8Z_c)]$ ;  $n_j \equiv (9/64)(RT_c)^2/P_c$ .

No. (j)	Name	$P(V,T)$	$a_j$	$Z_c$
(1)	Ideal Gas	$RT/V$	- Undefined -	
(2)	Van der Waals	$[RT/(V-b_2)] - a_2/V^2$	$3 n_2$	$= 3/8$
(3)	(translated) Van der Waals	$[RT/(V-b_3)] - a_3/(V+c_3)^2$	$3 n_3$	$> 1/4$
(4)	Berthelot	$[RT/(V-b_4)] - a_4/(TV^2)$	$3 n_4 T_c$	$= 3/8$
(5)	Clausius	$[RT/(V-b_5)] - a_5/[T(V+c_5)^2]$	$3 n_5 T_c$	$> 1/4$
(6)	Martin <sup>4</sup> (A)	$[RT/(V-b_6)] - a_6(4 T_c - T)/(V+c_6)^2$	$n_6/T_c$	$> 1/4$
(7)	Martin (B)	$[RT/(V-b_7)] - a_7(5 T_c - 2T)/(V+c_7)^2$	$n_7/T_c$	$> 1/4$

b. Same state equations {omitting No. (1)} in the reduced form  $\beta = (1/Z_c)\{[\gamma/(\eta-B)] - (9/8)A(\gamma)/(\eta+c)^2\}$ , where  $\beta = P/P_c$ ,  $\gamma = T/T_c$  and  $\eta = T/T_c$ . For all shown here,  $B = 1 - 1/(4Z_c)$ ,  $C = -1 + 3/(8Z_c)$  {independent of  $\gamma$ }, and  $X(\gamma) = 1/f(\gamma)$ .

No. (j)	$Z_c A(\gamma)$	$Z_c$	$f(\gamma)$	$\left(\frac{d\beta_A}{d\gamma}\right)_c \left\{ = \left(\frac{\partial\beta_A}{\partial\gamma}\right)_c \right\}$
(2)	$3/8$	$= 3/8$	1	4
(3)	$3/8$	$> 1/4$	1	4
(4)	$3/(8\gamma)$	$= 3/8$	$\gamma$	7
(5)	$3/(8\gamma)$	$> 1/4$	$\gamma$	7
(6)	$(4-\gamma)/8$	$> 1/4$	$3/(4-\gamma)$	5
(7)	$(5-2\gamma)/8$	$> 1/4$	$3/(5-2\gamma)$	6

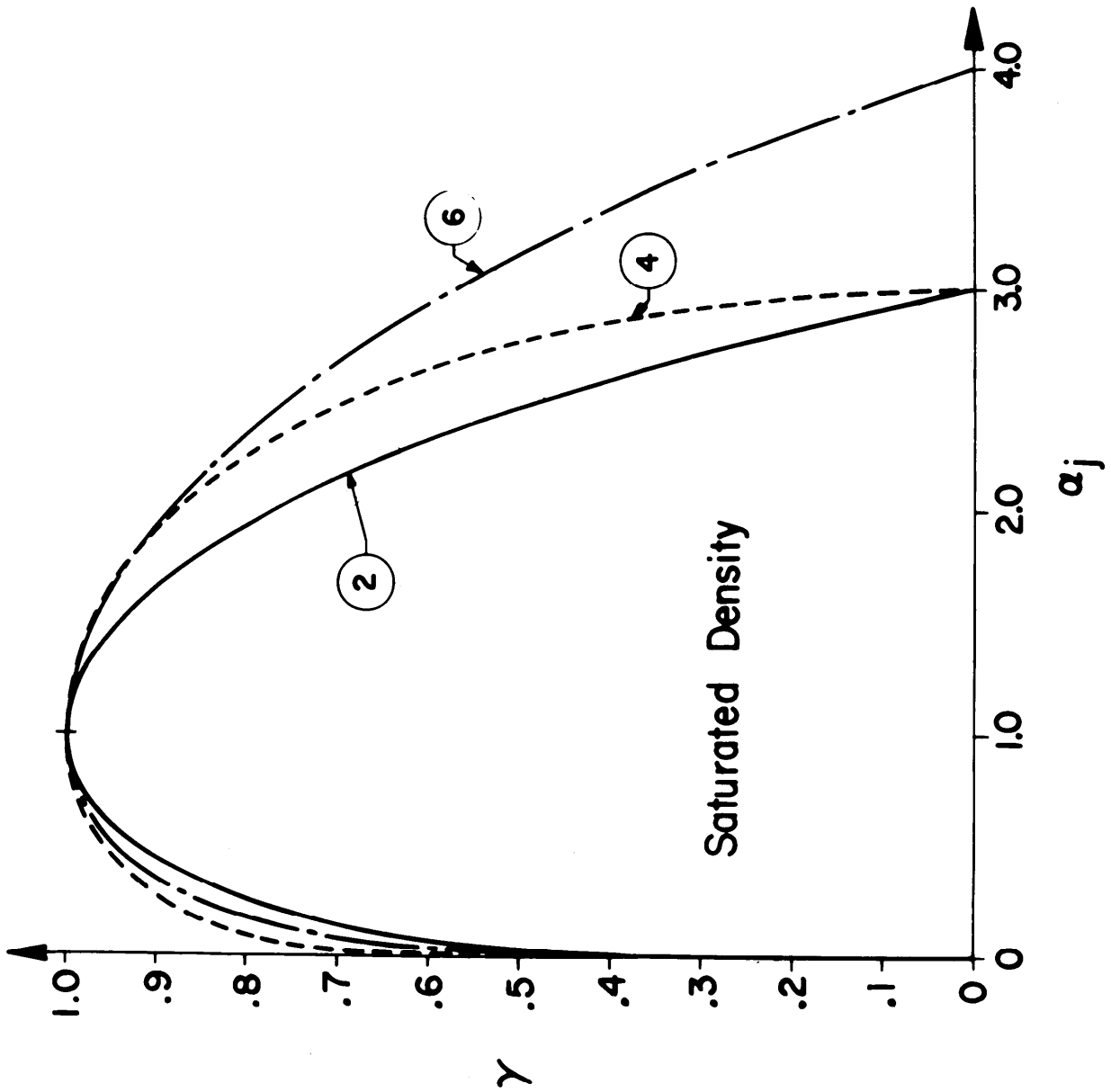


Figure 1. Reduced temperature vs. saturation densities. Numbers refer to state equations in Table I. For (6), the value of  $Z_c$  is assumed to be  $1/3$ .

Table I, using the given functions with Eq. (24); similar plots for examples 3 and 5 of Table I can easily be obtained from those of 2 and 4 respectively, when the value of  $C_1$  is assigned.

#### B. Vapor Pressure, ( $\gamma \leq 1$ ).

Eq. (26) gives the vapor pressure,  $\beta_A(\gamma)$ , as a function of  $w_A(u)$ , the [V-M] vapor pressure at the reduced temperature  $u$ , and the specific transforming function  $X(\gamma)$ . These are shown in Figure 2. For state equations having the same  $f(\gamma)$  functions and the same  $X(\gamma)$  functions, the vapor pressure is the same function of  $\gamma$ . Thus, the state equations numbered 2 and 3 in Table I have the same vapor pressure, as do those numbered 4 and 5.

#### C. Heat of Vaporization.

For  $T \leq T_c$ , the latent heat of vaporization  $\Delta Q_A(T)$  is found by using the Clapeyron relation,  $\Delta Q_A(T) = T \frac{dP_A}{dT} [V_1(T) - V_3(T)]$ ; in reduced variables this becomes

$$\Delta Q_A(T)/[RT_c] = Z_c \gamma \frac{d\beta_A}{d\gamma} [\eta_1(\gamma) - \eta_3(\gamma)] . \quad (29)$$

Using the inverse transformations,

$$\begin{aligned} \Delta Q_A(T)/[RT_c] = \{ \Delta Q_A(T)/[RT_c] \}_0 \left\{ \left( \frac{\partial u}{\partial \gamma} \right)_{\eta} / f^2(\gamma) \right\} \\ + \{ u w_A(u) [v_1(u) - v_3(u)] \} \left\{ Z_c A \frac{dX}{d\gamma} \right\} \end{aligned} \quad (30)$$

where the first factor on the right is the latent heat of vaporization for the [V-M] equation at the reduced temperature  $u$ . The functions  $w_A(u)$ ,  $v_1(u)$  and  $v_3(u)$  are also known; as with the vapor pressure function, the heat of vaporization is the same function of  $\gamma$  for state equations having the same  $f(\gamma)$  and  $X(\gamma)$ . Comparisons are shown in Figure 3; the values for the Berthelot and Clausius equations become



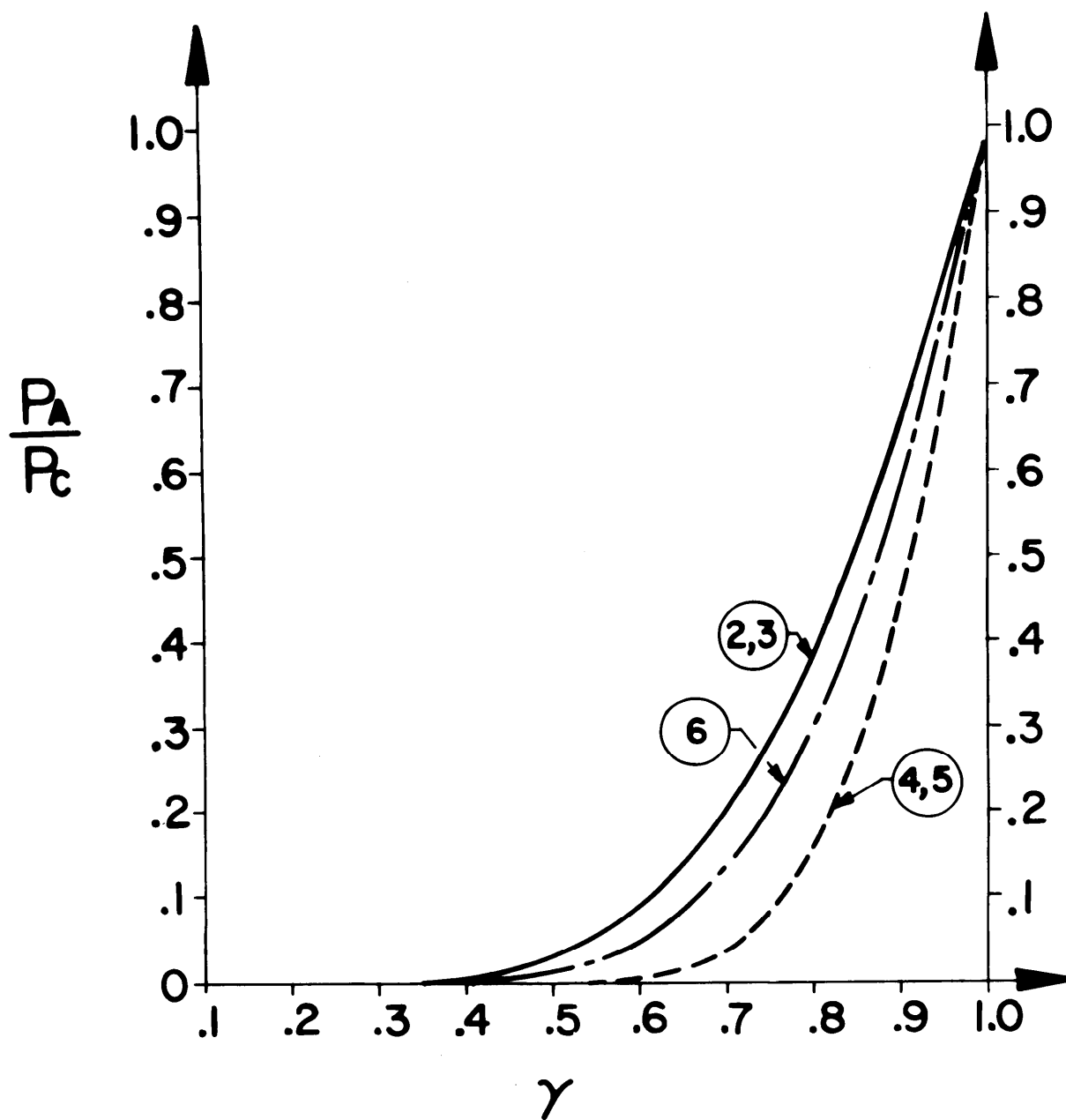


Figure 2. Vapor pressure vs. temperature for equations numbered in Table I. Vapor pressure is independent of  $Z_c$  for the examples shown.

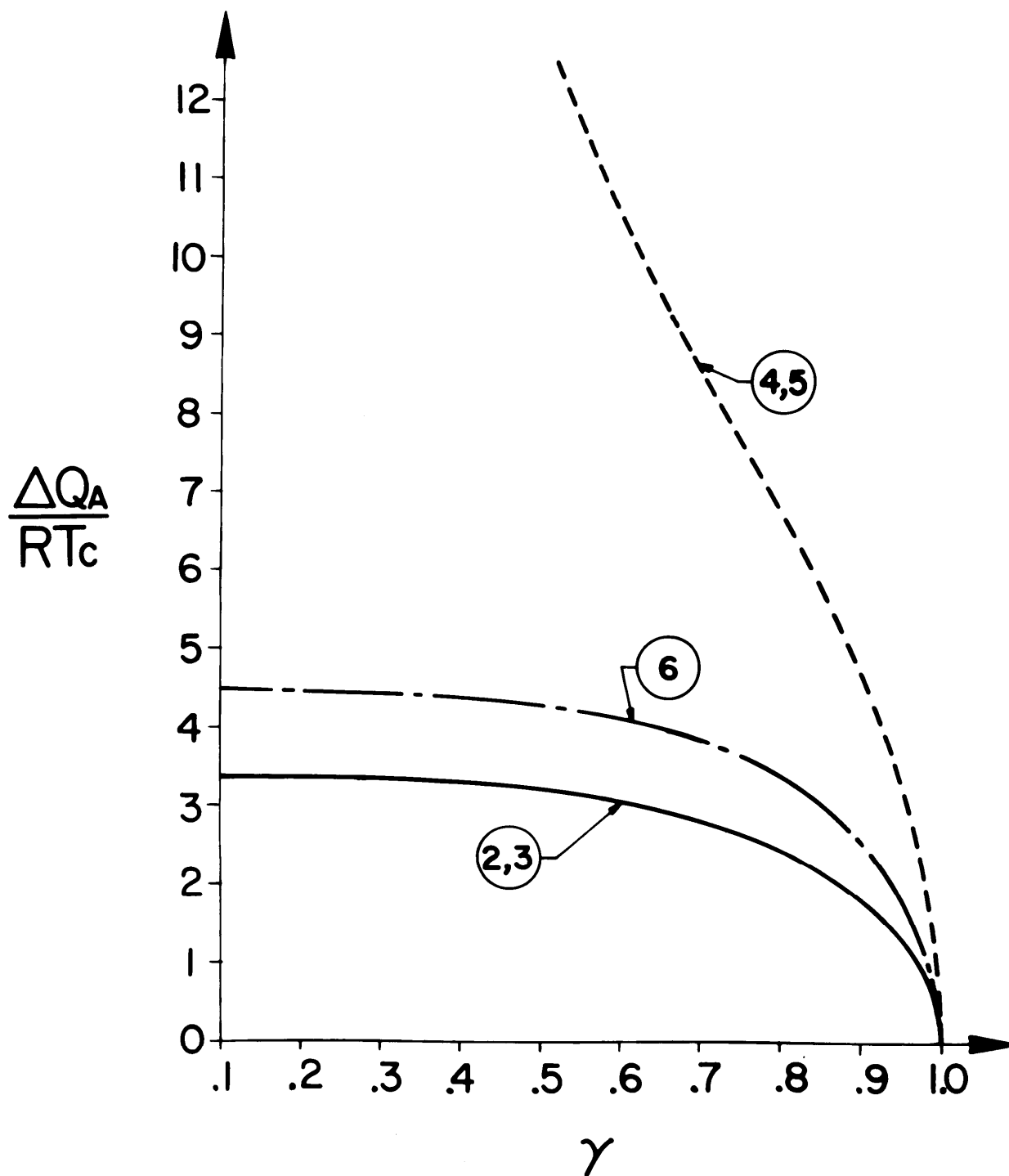


Figure 3. Latent heat of vaporization vs. reduced temperature for equations numbered in Table I. Latent heat is independent of  $Z_c$  for examples shown.

unrealistically large at small  $\gamma$ . Obviously,  $\Delta Q_A(T)$  vanishes at  $T = T_c$  for all equations. The entropy of vaporization,  $\Delta S_A(T)$ , is simply computed from  $\Delta Q_A(T)$  by using  $T \Delta S_A(T) = \Delta Q_A(T)$ .

D. Specific Heat at Constant Volume,  $C_v$ .

With  $E(V,T)$  the internal energy for unit mass (here taken to be the molar mass) the constant volume specific heat is  $C_v(V,T) = \left(\frac{\partial E}{\partial T}\right)_v$ , so that  $\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial^2 E}{\partial V \partial T}$ . The form of  $C_v$  within coexistence is  $C_{vA}(V,T)$ , and it differs from that of the single phase,  $C_{vB}(V,T)$ . By differentiating the thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v - P, \quad (31)$$

one obtains  $\frac{\partial^2 E}{\partial T \partial V} = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v$ ; using reduced variables and equating the above mixed derivatives, one gets:

$$\frac{\partial (C_{vB}/R)}{\partial \eta} = \gamma Z_c \left(\frac{\partial^2 \beta_B}{\partial \gamma^2}\right)_\eta. \quad (32)$$

Performing a partial integration with respect to  $\eta$ , one obtains

$$C_{vB}(\eta, \gamma)/R = C_v^0(\gamma)/R + \gamma F(\eta, \gamma) \quad (33)$$

where, with a prime hereafter signifying  $\left(\frac{d}{d\gamma}\right)$ ,

$$F(\eta, \gamma) = \{(9/8)/[\eta + C(\gamma)]^3\} \{A''[\eta + C(\gamma)]^2 - [2A'C' + AC''][\eta + C(\gamma)] + 2A(C')^2\}. \quad (34)$$

Here  $C_v^0(T)$  is the specific heat of the single phase at very low density  $\{\eta \rightarrow \infty, F(\eta, \gamma) \rightarrow 0\}$ ; for a monatomic vapor at moderate temperature  $C_v^0(T)$  is  $3R/2$ . Since  $C_{vB}$  must always be positive in the single phase,

further restrictions are imposed on the permissible functions  $A(\gamma)$  and  $C(\gamma)$ . It is for this reason that  $B$  is forced to be a constant rather than a function of  $\gamma$ , as shown in the Appendix. Because  $Z_c \frac{\partial^2 \beta_A}{\partial \gamma^2} = \left( \frac{\partial F}{\partial \eta} \right)_\gamma$ , from Eq. (34) one obtains,

$$Z_c \frac{\partial^2 \beta_A}{\partial \gamma^2} = \{ (9/8) / [\eta + C(\gamma)]^4 \} \{ -A'' [\eta + C(\gamma)]^2 + 2[2A'C' + AC''] [\eta + C(\gamma)] - 6A(C')^2 \}. \quad (35)$$

If  $C'(\gamma)$  and  $A''(\gamma)$  are identically zero, then  $\frac{\partial^2 \beta_A}{\partial \gamma^2}$  and  $F(\eta, \gamma)$  are identically zero in the single phase.

Within coexistence,  $T \leq T_c$ ,  $V_3(T) \leq V_1(T)$ , the specific heat is  $C_{V_A}(V, T)$ ; it can be found by using  $E_A(V, T)$  and  $P_A(V, T)$  in Eq. (31), integrating it at fixed  $T \leq T_c$  from  $V_3(T)$  to some  $V$  within coexistence, and differentiating the result by  $T$ . Both  $E_A(V, T)$  and  $C_{V_A}(V, T)$  are linear functions of  $V$ . Using the fact that the internal energy and pressure functions are continuous across the boundary of coexistence, one can obtain in reduced variables

$$\{C_{V_A}(V, T) - C_V^0(T)\} / R = \Gamma(\eta, \gamma), \quad (36)$$

where

$$\Gamma(\eta, \gamma) = \gamma \eta_3'(\gamma) \left\{ \left( \frac{\partial \beta_A}{\partial \gamma} \right)_{\eta=\eta_3} - \beta_A'(\gamma) \right\} + \gamma F(\eta_3, \gamma) + \gamma \beta_A''(\gamma) [\eta - \eta_3(\gamma)]. \quad (37)$$

In general  $\left( \frac{\partial \beta_A}{\partial \gamma} \right)_\eta$  is not equal to  $\beta_A'(\gamma)$  at  $(\eta_3, \gamma)$ , so the constant volume specific heat exhibits a discontinuity across the coexistence boundary.

Recalling that the  $\xi_j$  are functions of  $u$ , one can use the inverse transformations and arrange the terms to obtain:

$$\Gamma(\eta, \gamma) = \{\Gamma(v, u)\}_0 k_1(\gamma) + (3-\xi_3)(\xi_3-\xi_1)\{k_2(\gamma) - (3-2\xi_3-\xi_1)k_3(\gamma)\} \quad (38)$$

$$+ \{(\xi_3-\xi)/(\xi_3\xi)\}\{u \frac{dw_A}{du} k_4(\gamma) + uw_A k_5(\gamma)\} + \gamma F_2(\xi_3, \gamma).$$

Here the  $k_i$  are functions of  $\gamma$ , and:

$$\begin{aligned} k_1 &\equiv \{u'/f\}^2; & k_2 &\equiv 6Z_c u' C' X/f \\ k_3 &\equiv 3Z_c X [C']^2 / [f^2 A]; & k_4 &\equiv AZ_c [Xu'' + 2X'u'] \\ k_5 &\equiv AZ_c X''; \text{ and with } m = \xi_3/[fA], \end{aligned}$$

$$F_2(\xi_3, \gamma) = (9/8) m \{A'' - [2A'C' + AC''] m + 2A[C']^2 m^2\}.$$

$\{\Gamma(v, u)\}_0$  is the corresponding quantity for the [V-M] system at the point  $(v, u)$  inside coexistence. The value of  $\Gamma(\eta, \gamma)$  at the critical point is easily found because both  $\xi$  and  $\xi_1$  become equal to  $\xi_3$  there, and the second and third terms vanish. The critical value of  $\{\Gamma(1, 1)\}_0$  is known to be 4.5, and neither  $k_1(\gamma)$  nor  $F_2(1, 1)$  is infinite there. Therefore,  $\Gamma(\eta, \gamma)$  is always finite at the critical point, and state equations of this class cannot show an infinite  $C_{vA}$  here, as suggested by some experimental data. Along the saturated liquid locus ( $\xi = \xi_3$ ), the third term of Eq. (38) vanishes. When  $C' \equiv 0$  (as happens for all example equations in Table I), Eq. (38) simplifies along the saturated liquid locus,  $(\eta_3, \gamma)$ , to:

$$\Gamma(\eta_3, \gamma) = \{\Gamma(v_3, u)\}_0 \{u'/f\}^2 + (9/8) \xi_3(u) \{\gamma A''/[fA]\}. \quad (39)$$

#### E. Vaporizing Signal Speed

The speed of a small amplitude adiabatic expansion wave (with partial vaporization) propagating into the saturated liquid<sup>5</sup> is denoted by  $a_A(V_3, T)$ , and is equal to  $V_3 \frac{dP_A}{dT} \{T/C_{vA}(V_3, T)\}^{\frac{1}{2}}$ ; in reduced notation,

$$a_A(V_3, T)/[RT_c]^{1/2} = z_c \eta_3 \frac{d\beta_A}{d\gamma} \{ \gamma / [\Gamma(\eta_3, \gamma) + C_V^0/R] \}^{1/2}. \quad (40)$$

A comparison of these speeds is shown in Figure 4 for the sample equations numbered 2, 4, and 6 in Table I, with the assumption that  $C_V^0/R$  is 3/2. The limiting values at the critical point for certain coexistence properties of sample state equations are shown in Table II.

#### IV. DISCUSSION

The predicted thermodynamic properties of coexistence for this class of elementary state equations are seen to be conveniently done in terms of the known [V-M] system. The use of different functions  $A(\gamma)$ ,  $B$  and  $C(\gamma)$ , might improve the agreement between prediction and observation. However, this class of state equation contains one serious drawback in the critical region which cannot be overcome by modifying these functions. This defect is that this entire class predicts  $|P-P_c|$  to vary as the third power of  $|V-V_c|$  on the critical isotherm; recent data suggests that this exponent is larger than three<sup>6</sup>, and perhaps as large as five<sup>7</sup>. With this restriction, however, this class equation is useful in giving a qualitative survey of some subcritical transition properties of liquids and gases.

Table II. Critical point values for designated quantities  
State equation numbers correspond to those  
of Table I. Value of  $C_v^0$  was assumed  
 $3R/2$  to compute last column.

Equation No.	$\frac{d^2 \beta_A}{d\gamma^2}$	$\frac{\partial^2 \beta_B}{\partial \gamma^2}$	$(C_{vA} - C_v^0)/R$	$(C_{vB} - C_v^0)/R$	$a_A/(RT_c)^{\frac{1}{2}}$
2	$9 \frac{3}{5}$	0	$4 \frac{1}{2}$	0	.612
3	$9 \frac{3}{5}$	0	$4 \frac{1}{2}$	0	1.633 $Z_c$
4	$32 \frac{2}{5}$	-6	$20 \frac{1}{4}$	$2 \frac{1}{4}$	.563
5	$32 \frac{2}{5}$	-6	$20 \frac{1}{4}$	$2 \frac{1}{4}$	1.501 $Z_c$
6	$17 \frac{2}{5}$	0	8	0	1.622 $Z_c$
7	$26 \frac{2}{3}$	0	$12 \frac{1}{2}$	0	1.871 $Z_c$

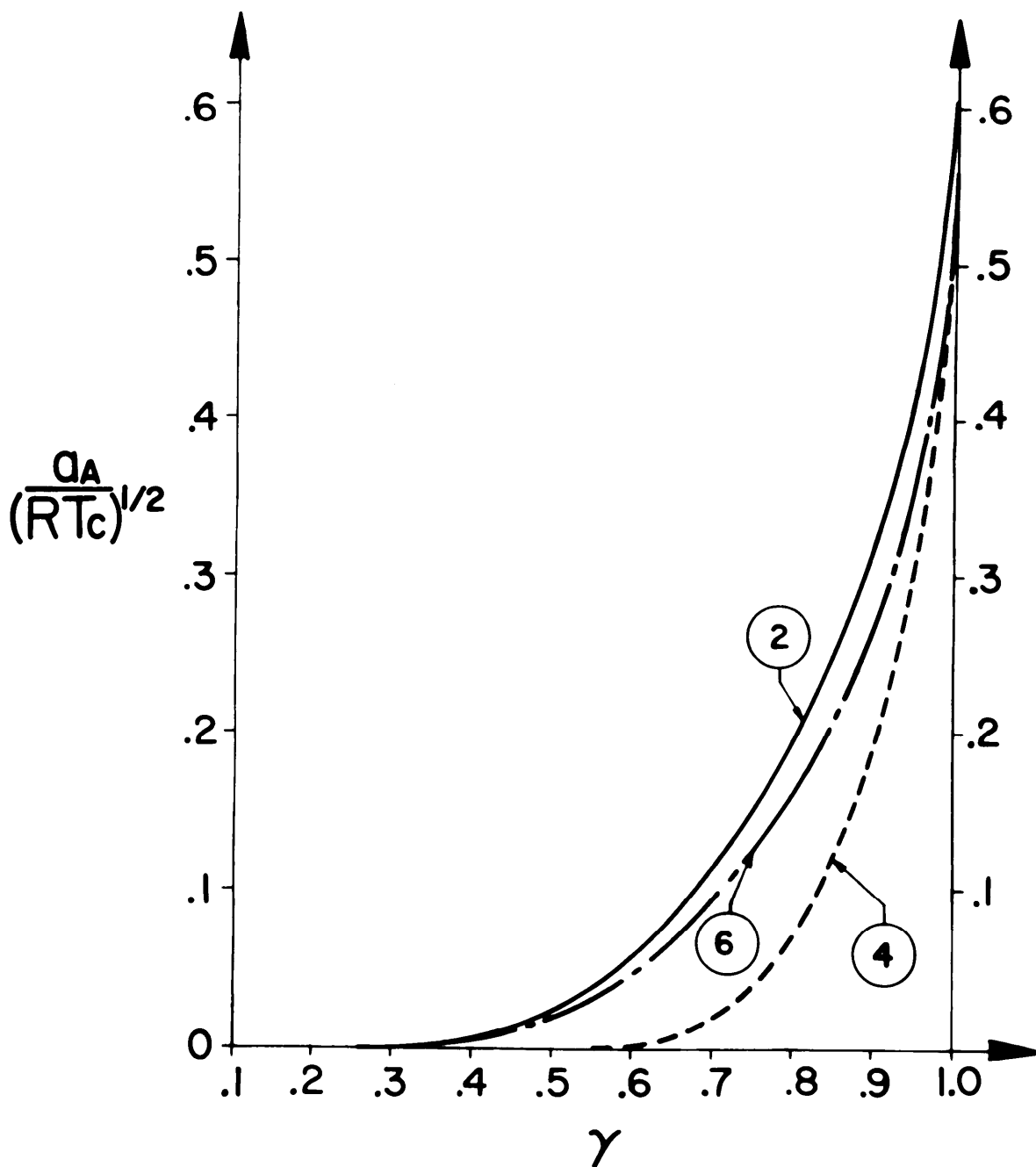


Figure 4. Vaporizing signal speed of the saturated liquid for equations numbered in Table I. The curve shown for No. 6 was computed for  $Z_c = 1/3$ . The value  $3R/2$  was used for  $C_v^0$ .



# FOOTNOTES AND REFERENCES

1. R. E. Barieau, Phys. Rev. Letters 16, 297 (1966).
2. L. D. Landau and E. M. Lifshitz, Statistical Physics, Pergamon Press, Ltd., London, (1958), pp. 60-62, 262-264.
3. R. B. Griffiths, Phys. Rev. 158, 176 (1967), especially Appendix B.
4. J. J. Martin, Ind. and Eng. Chem. 59, 34 (Dec. 1967).
- \* Martin uses the forms {his Eq. (28) in present notation}  
 $A(\gamma) = (4-\gamma)/8Z_c$ ,  $B = .085/Z_c$  and  $C(\gamma) = .04/Z_c$ , and cautions that  
the critical conditions,  $\gamma = \beta = 1$ ,  $\frac{\partial \beta}{\partial \eta} = \frac{\partial^2 \beta}{\partial \eta^2} = 0$ , will hold only  
for  $Z_c = .335$ . He sometimes gives up these critical conditions to  
obtain a better overall fit to experimental P, V, T data outside  
coexistence. A. V. Grosse uses this same form with  $Z_c = .27$  to  
describe approximately the properties of cesium, {Inorg. Nucl.  
Chem. Letters 4, 261 (1968)}.
5. F. D. Bennett, Phys. Fluids 8, 1425 (1965).
6. L. P. Kadanoff, et. al., Rev. Mod. Phys. 39, 395 (1967).
7. M. S. Green, M. Vicentini-Missoni, J. M. H. Levelt Sengers,  
Phys. Rev. Letters 18, 1113 (1967).

## APPENDIX

### I. Showing B must be Independent of $\gamma$

If B were allowed to be a function of  $\gamma$ , there would be additional terms in  $C_{VB}(V,T)$  of Eq. (33). These extra terms would be

$$- \left\{ (9/8) R\gamma/(\eta-B) \right\} \left\{ 2B' + \gamma(B')^2/(\eta-B) \right\}.$$

Since  $\eta$  can approach B in the single phase of this fluid, the last term would contribute a dominant negative value to  $C_{VB}(V,T)$ , unless  $B'(\gamma)$  were identically zero. Because of the stability condition  $C_V(V,T) > 0$ , it is then necessary that  $B(\gamma)$  be a constant. Restrictions are also required on  $A(\gamma)$  and  $C(\gamma)$ , but they are not as simple. With  $x = [\eta + C(\gamma)]^{-1}$ , and the definitions  $L(\gamma) \equiv 2A''(\gamma)$ ,  $M(\gamma) \equiv 2A'C' + AC''$  and  $N(\gamma) \equiv 2AC''$ , then Eq. (33) becomes

$$C_{VB}/R = C_V^0/R + (9/8) \gamma x \{ L(\gamma) - xM(\gamma) + x^2N(\gamma) \}, \quad (A-1)$$

where, for  $\gamma \leq 1$ , the permissible  $x$  range over a positive interval from 0 to  $x_1 = + [B + C(\gamma)]^{-1} < +\infty$ ; for  $\gamma \geq 1$ , permissible values of  $x$  range over a similar interval, excluding, however, a sub-interval corresponding to  $\eta$  values within the coexistence region. {For this sub-interval, the proper expression for  $C_V$  is  $C_{VA}$ , given by Eq. (36)}. Eq. (A-1) is a cubic polynomial in  $x$ , and can have a variety of shapes, depending on the coefficients  $L(\gamma)$ ,  $M(\gamma)$  and  $N(\gamma)$ . The functions  $A(\gamma)$  and  $B(\gamma)$  must be restricted so  $C_V$  is always positive. This requirement is satisfied for all the example equations shown in Table I.

### II. Reduced Variables for the [V-M] Fluid

The set of values given in Table III for the [V-M] system can be used with the transformation equations to compare easily the sub-critical

Table III. Reduced values of coexistence temperature,  
saturation densities, and vapor  
pressure for the Van der Waals-  
Maxwell state equation

<u>u</u>	<u><math>\xi_3</math></u>	<u><math>\xi_1</math></u>	<u><math>w_A</math></u>
1.000	1.0000	1.0000	1.0000
.998	1.0902	.91140	.99202
.994	1.1571	.84773	.97617
.990	1.2035	.80454	.96048
.98	1.2894	.72669	.92191
.97	1.3558	.66844	.88429
.96	1.4121	.62042	.84762
.95	1.4617	.57901	.81188
.93	1.5482	.50931	.74318
.90	1.6573	.42574	.64700
.85	1.8071	.31973	.50449
.80	1.9327	.23967	.38336
.75	2.0424	.17721	.28246
.70	2.1404	.12802	.20046
.65	2.2296	.89475x10 <sup>-1</sup>	.13584
.60	2.3116	.59778x10 <sup>-1</sup>	.86869x10 <sup>-1</sup>
.55	2.3875	.37580x10 <sup>-1</sup>	.51580x10 <sup>-1</sup>
.50	2.4585	.21747x10 <sup>-1</sup>	.27789x10 <sup>-1</sup>
.45	2.5251	.11217x10 <sup>-1</sup>	.12134x10 <sup>-1</sup>
.40	2.5879	.49109x10 <sup>-2</sup>	.51745x10 <sup>-2</sup>
.35	2.6475	.16875x10 <sup>-2</sup>	.15673x10 <sup>-2</sup>
.30	2.7042	.39907x10 <sup>-3</sup>	.31882x10 <sup>-3</sup>
.25	2.7583	.51259x10 <sup>-4</sup>	.34165x10 <sup>-4</sup>
.20	2.8012	.22296x10 <sup>-5</sup>	.11891x10 <sup>-5</sup>
.15	2.8602	.41565x10 <sup>-7</sup>	.43602x10 <sup>-8</sup>
.10	2.9083	.21612x10 <sup>-12</sup>	.57631x10 <sup>-13</sup>
.04	2.9640	.56824x10 <sup>-34</sup>	.60612x10 <sup>-35</sup>
0.00	3.0000	0.00	0.00

thermodynamic predictions for any state equation belonging to this class. Five significant figures are given for every function except  $u$ , which is assumed to be exact. These values were computed at this laboratory with the assistance of D. C. Mylin and F. H. MacIntosh. R. Barieau<sup>1</sup> gives a much more extensive tabulation of various thermodynamic properties for the [V-M] fluid for  $.25 \leq u \leq 1.0$ . For these  $u$ , the above values agree with his tabulations.

# DISTRIBUTION LIST

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
20	Commander Defense Documentation Center ATTN: TIPCR Cameron Station Alexandria, Virginia 22314	1	Commanding Officer U.S. Army Picatinny Arsenal ATTN: SMUPA-V Mr. E. Walbrecht Dover, New Jersey 07801
1	Commanding General U.S. Army Materiel Command ATTN: AMCRD-TE Washington, D. C. 20315	1	Commanding Officer U.S. Army Harry Diamond Laboratories Washington, D. C. 20438
1	Commanding General U.S. Army Materiel Command ATTN: AMCRD-TC Washington, D. C. 20315	1	Commandant U.S. Army Logistics Management Center Fort Lee, Virginia 23801
1	Commanding General U.S. Army Materiel Command ATTN: AMCRD-TP Washington, D. C. 20315	1	Commanding Officer U.S. Army Materials and Mechanics Research Center Watertown, Massachusetts 02172
1	Commanding General U.S. Army Materiel Command ATTN: AMCRD-BN Washington, D. C. 20315	1	Commanding General U.S. Army Natick Labs Natick, Massachusetts 01762
2	Commanding General U.S. Army Missile Command ATTN: AMSMI-RBL Redstone Arsenal, Alabama 35809	1	Director U.S. Army Nuclear Defense Laboratory Edgewood Arsenal, Maryland 21010
1	Commanding Officer U.S. Army Mobility Equipment Research & Development Center ATTN: Tech Docu Ctr, Bldg 315 Fort Belvoir, Virginia 22060	1	Commanding Officer U.S. Army Foreign Science & Technology Center Munitions Building Washington, D. C. 20315
2	Commanding Officer U.S. Army Frankford Arsenal ATTN: SMUFA-N1000 Mr. C. Lukens SMUFA-C2500 Philadelphia, Pennsylvania 19137	1	Commanding Officer U.S. Army Terrestrial Sciences Center Hanover, New Hampshire 03755

# DISTRIBUTION LIST

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	Commanding Officer U.S. Army Satellite Communications Agency Fort Monmouth, New Jersey 07703	1	Commander U.S. Naval Weapons Center ATTN: Code 753 China Lake, California 93555
1	Commanding Officer U.S. Army Maintenance Board Fort Knox, Kentucky 40121	2	Commander U.S. Naval Ordnance Lab ATTN: Code 730, Lib Code 242, Mr. Leopold Silver Spring, Maryland 20910
1	Commanding General U.S. Army Combat Developments Command ATTN: CDCMR-W Fort Belvoir, Virginia 22060	1	Superintendent U.S. Naval Postgraduate School ATTN: Tech Reprt Sec Monterey, California 20910
1	Chief of Staff ATTN: CSAVCS-W-TIS Department of the Army Washington, D. C. 20301	3	Director U.S. Naval Research Lab ATTN: Code 7700, Dr. A. Kolb Code 7720, Dr. E. McLean Mr. I. Vitkovitsky Washington, D. C. 20390
1	Director U.S. Army Research Office 3054 Columbia Pike Arlington, Virginia 22204	1	Commander U.S. Naval Weapons Laboratory Dahlgren, Virginia 22448
1	Commanding Officer U.S. Army Research Office (Durham) Box CM, Duke Station Durham, North Carolina 27706	1	ADTC (ADBPS-12) Eglin AFB Florida 32542
3	Commander U.S. Naval Air Systems Command ATTN: AIR-604 Washington, D. C. 20360	1	ADTC (ADOW) Eglin AFB Florida 32542
3	Commander U.S. Naval Ordnance Systems Command ATTN: ORD-9132 Washington, D. C. 20360	1	AFATL (ATW) Eglin AFB Florida 32542
		1	AFWL (WLRE, Dr. Guenther) Kirtland AFB New Mexico 87117

# DISTRIBUTION LIST

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
1	ESD (ESTI) L.G. Hanscom Field Bedford, Massachusetts 01731	1	Director National Aeronautics and Space Administration Electronic Research Center ATTN: Dr. V. Scherrer 575 Technology Square Cambridge, Massachusetts 02139
1	AFAL (AVW) Wright-Patterson AFB Ohio 45433		
1	AUL (3T-AUL-60-118) Maxwell AFB Alabama 36112	1	Director National Aeronautics and Space Administration Langley Research Center ATTN: Code 04.000 Langley Station Hampton, Virginia 23365
3	Director National Bureau of Standards ATTN: Code 164, Dr. D. Tsai Mr. P. Krupenie Mr. J. Park U.S. Department of Commerce Washington, D.C. 20325	1	Director National Aeronautics and Space Administration Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135
1	Headquarters U.S. Atomic Energy Commission ATTN: Lib Br Washington, D.C. 20545	1	Director Jet Propulsion Laboratory ATTN: Mr. I. Newlan 4800 Oak Grove Drive Pasadena, California 91103
1	Director Lawrence Radiation Laboratory ATTN: Dr. C. Olsen P.O. Box 808 Livermore, California 94550	1	Director Smithsonian Astrophysical Observatory 60 Garden Street Cambridge, Massachusetts 02138
2	Director Los Alamos Scientific Laboratory ATTN: Dr. R. Reithel Dr. J. L. Tuck P.O. Box 1663 Los Alamos, New Mexico 87544	1	Aerojet-General Corporation ATTN: Dr. G. Woffinden 11711 South Woodruff Avenue Downey, California 90241
1	Director NASA Scientific and Technical Information Facility ATTN: SAK/DL P.O. Box 33 College Park, Maryland 20740	1	Atlantic Research Corporation ATTN: Mr. A. Macek Shirley Highway at Edsall Road Alexandria, Virginia 22314

# DISTRIBUTION LIST

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
2	AVCO-Everett Research Laboratory ATTN: Tech Lib Dr. G. Sargent James 2385 Revere Beach Parkway Everett, Massachusetts 02149	3	Sandia Corporation ATTN: Dr. E. Cnare Dr. F. Neilson Dr. T. Tucker P.O. Box 5800 Albuquerque, New Mexico 87115
1	E. I. duPont de Nemours and Company Eastern Laboratory Library ATTN: Miss M. Imbrie Gibbstown, New Jersey 08027	2	Sandia Corporation ATTN: Mr. J. R. Hearst Bldg T105 Dr. G. Anderson P.O. Box 969 Livermore, California 94551
1	Fairchild Hiller Republic Aviation Division ATTN: Engr Lib Farmingdale, New York 11735	1	Willow Run Laboratories P.O. Box 2008 Ann Arbor, Michigan 48105
2	Field Emission Corporation ATTN: Mr. F. Collins Dr. J. Trolan McMinnville, Oregon 97128	1	Arizona State University ATTN: Prof R. Stoner Tempe, Arizona 85281
1	General Electric Research Laboratory ATTN: Dr. R. Alpher P.O. Box 1088 Schenectady, New York 12305	1	University of Arkansas Department of Physics Fayetteville, Arkansas 72701
1	General Electric Company Space Sciences Laboratory ATTN: Dr. R. Good, Jr. P.O. Box 8555 Philadelphia, Pennsylvania 19101	1	California Institute of Technology Guggenheim Aeronautical Lab ATTN: Prof L. Lees Pasadena, California 91104
1	Hughes Aircraft Company Systems Development Laboratory ATTN: Dr. A. Puckett Centinela and Teale Streets Culver City, California 90230	1	California Institute of Technology Aeronautics Department ATTN: Prof H. Liepmann 1201 East California Blvd Pasadena, California 91102
1	Lockheed Missile & Space Co. 3251 Hanover Street Palo Alto, California 94304	1	Case Institute of Technology Department of Mechanical Engineering ATTN: Prof G. Kuerti 10900 Euclid Avenue Cleveland, Ohio 44106



# DISTRIBUTION LIST

<u>No. of Copies</u>	<u>Organization</u>	<u>No. of Copies</u>	<u>Organization</u>
1	University of California Department of Chemistry ATTN: Dr. G. Nash Davis, California 95616	1	The Johns Hopkins University Department of Mechanics ATTN: Prof L. Kovasznay 34th and Charles Streets Baltimore, Maryland 21218
1	Columbia University ATTN: Prof R. Gross 236 Seeley W. Mudd Building New York, New York 10027	1	Lehigh University Department of Physics ATTN: Prof R. Emrich Bethlehem, Pennsylvania 18015
1	University of Colorado Joint Institute for Laboratory Astrophysics ATTN: Prof R. Thomas 1511 University Avenue Boulder, Colorado 80302	2	University of Maryland Institute of Fluid Dynamics and Applied Mathematics ATTN: Prof J. Burgers Prof S. Pai College Park, Maryland 20740
1	Cornell University Graduate School of Aeronautical Engineering ATTN: Prof E. Resler Ithaca, New York 14850	1	Massachusetts Institute of Technology Aerophysics Laboratory Cambridge, Massachusetts 02139
1	Cornell Aeronautical Laboratory, Inc. ATTN: Lib Dr. G. Shinner P.O. Box 235 Buffalo, New York 14221	1	University of Michigan Department of Physics ATTN: Prof O. Laporte Ann Arbor, Michigan 48104
1	Harvard University ATTN: Prof H. Emmons Cambridge, Massachusetts 02138	1	University of Michigan Department of Aeronautical & Astronautical Engineering ATTN: Prof M. Sichel Ann Arbor, Michigan 48104
1	University of Illinois Department of Aeronautical Engineering ATTN: Prof R. Strehlow Urbana, Illinois 61803	1	North Carolina State University at Raleigh ATTN: Dr. Tien S. Chang 325 Riddick Laboratories Raleigh, North Carolina 27607
1	Director Applied Physics Laboratory The Johns Hopkins University 8621 Georgia Avenue Silver Spring, Maryland 20910	1	Oklahoma City University Department of Physics ATTN: Prof. M. Coffman Oklahoma City, Oklahoma 73100

# DISTRIBUTION LIST

<u>No. of Copies</u>	<u>Organization</u>	<u>No. of Copies</u>	<u>Organization</u>
1	University of Oklahoma Department of Physics ATTN: Prof R. Fowler Norman, Oklahoma 73069	1	Stanford University Department of Mechanical Engineering ATTN: Prof D. Bershader Stanford, California 94305
1	Princeton University Department of Aerospace and Mechanical Sciences ATTN: Prof W. D. Hayes Princeton, New Jersey 08540	1	Stevens Institute of Technology Department of Electrical Engineering ATTN: Prof R. Geldmacher Castle Point Station Hoboken, New Jersey 07030
1	Princeton University Forrestal Research Center ATTN: Prof S. Bogdonoff Princeton, New Jersey 08540	2	Research Institute of Temple University ATTN: Dr. A. V. Grosse Tech Lib 4150 Henry Avenue Philadelphia, Pennsylvania 19144
1	Princeton University Palmer Physical Laboratory ATTN: Prof W. Bleakney Princeton, New Jersey 08540		
			<u>Aberdeen Proving Ground</u> Ch, Tech Lib Air Force Ln Ofc Marine Corps Ln Ofc Navy Ln Ofc CDC Ln Ofc

Unclassified

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

<b>1. ORIGINATING ACTIVITY (Corporate author)</b> U.S. Army Aberdeen Research and Development Center Ballistic Research Laboratories Aberdeen Proving Ground, Maryland		<b>2a. REPORT SECURITY CLASSIFICATION</b> Unclassified	
		<b>2b. GROUP</b>	
<b>3. REPORT TITLE</b>  A CLASS OF TWO-PHASE STATE EQUATIONS			
<b>4. DESCRIPTIVE NOTES (Type of report and inclusive dates)</b>			
<b>5. AUTHOR(S) (First name, middle initial, last name)</b>  George D. Kahl			
<b>6. REPORT DATE</b> March 1969		<b>7a. TOTAL NO. OF PAGES</b> 38	<b>7b. NO. OF REFS</b> 7
<b>8a. CONTRACT OR GRANT NO.</b>		<b>9a. ORIGINATOR'S REPORT NUMBER(S)</b>	
<b>b. PROJECT NO.</b> 1T061102A33D		Report No. 1429	
<b>c.</b>		<b>9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)</b>	
<b>d.</b>			
<b>10. DISTRIBUTION STATEMENT</b>  This document has been approved for public release and sale; its distribution is unlimited.			
<b>11. SUPPLEMENTARY NOTES</b>		<b>12. SPONSORING MILITARY ACTIVITY</b>  U. S. Army Materiel Command Washington, D. C.	
<b>13. ABSTRACT</b>  The properties of a particular class of elementary, two-phase state equations are found to be simply related. The class includes some familiar equations, such as the Van der Waals, Berthelot, and Clausius types, as well as a form recently suggested by J. J. Martin. Conditions for stable equilibrium are given, and some examples are compared. A table of values is included which can be used with elementary transformations to find the equilibrium coexistence properties of any member of the set. A drawback for this type equation along the critical isotherm is noted.			

DD FORM 1473

NOV 65

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified

Security Classification

Unclassified

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Tw-Phase State Equation Van der Waals Berthelot Clausius Martin Equilibrium Coexistence						

Unclassified

Security Classification